Soil Chemistry: pH

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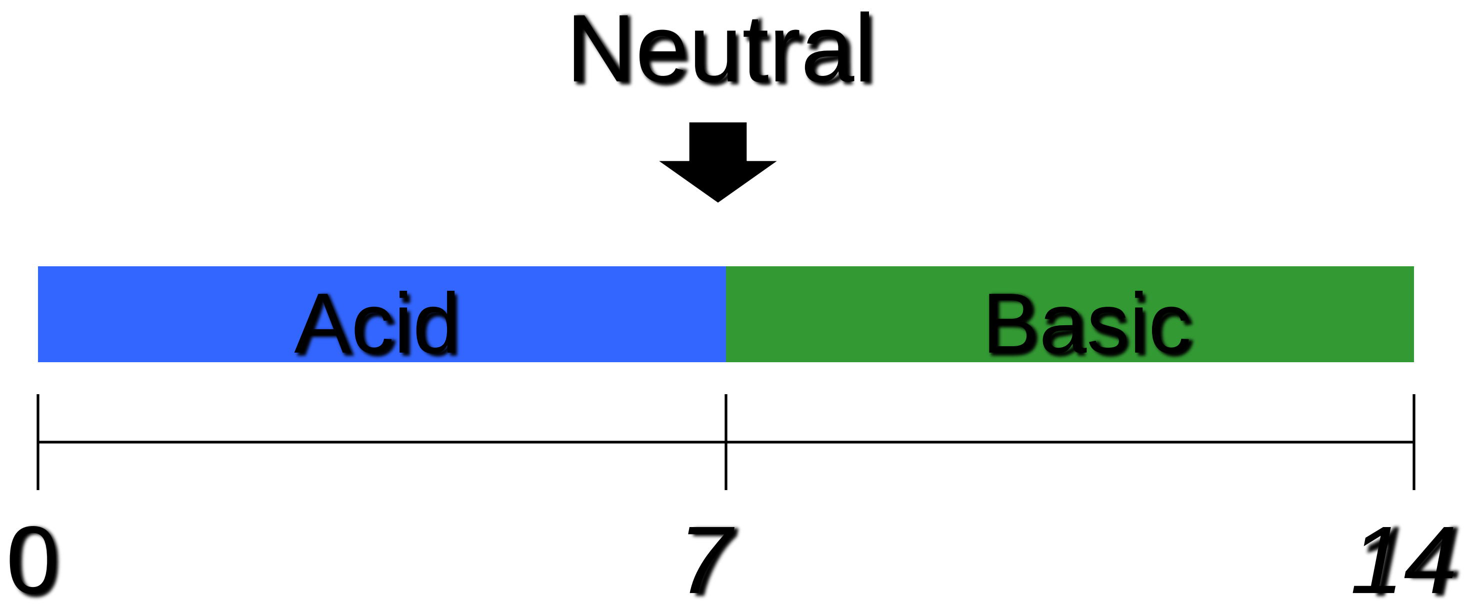
- What is pH?
- Why do we care?
- How do we measure it?
  - Soil
  - Lime Requirement
  - Water

pH

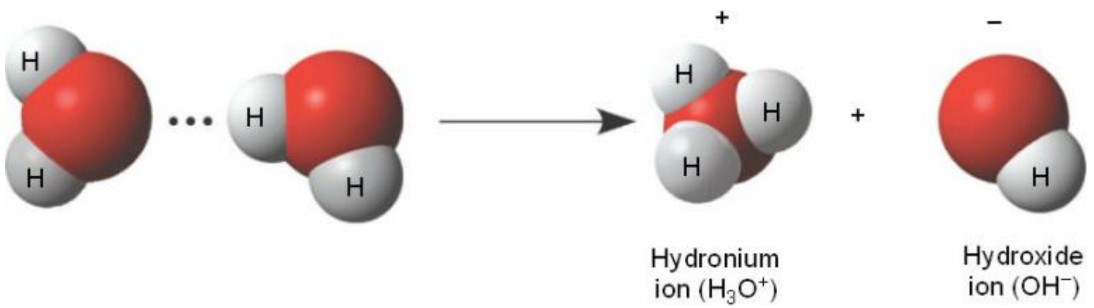
- pH is the negative logarithm of the hydrogen(proton)/hydronium ion activity (not concentration)
  - $pH = -\log (H^+)$
  - Concentration and activity are often similar in value
  - Unlike concentration, activity does not have units and, therefore, neither does pH

pH range is 0 to 14



pH is based on dissociation of water

- In any volume of water, most of it is the H2O molecule, but some of it is dissociated as follows:
  - $H_2O \leftrightarrow H^+ + OH^-$
  - However, H^- . . .



Logarithm

$pH = -\log(H^+)$

(factor of 10)

Inversely Related

pH	(H^+) activity
0	1.0
1	0.1
2	0.01
3	0.001
4	0.0001
5	0.00001
6	0.000001
7	0.0000001
8	0.00000001
9	0.000000001
10	0.0000000001
11	0.00000000001
12	0.000000000001
13	0.0000000000001
14	0.00000000000001

pH	(OH^-) activity
14	1.0
13	0.1
12	0.01
11	0.001
10	0.0001
9	0.00001
8	0.000001
7	0.0000001
6	0.00000001
5	0.000000001
4	0.0000000001
3	0.00000000001
2	0.000000000001
1	0.0000000000001
0	0.00000000000001

At neutral pH 7, they are equal

pH	(H^+) activity
0	1.0
1	0.1
2	0.01
3	0.001
4	0.0001
5	0.00001
6	0.000001
7	0.0000001
8	0.00000001
9	0.000000001
10	0.0000000001
11	0.00000000001
12	0.000000000001
13	0.0000000000001
14	0.00000000000001

pH	(OH^-) activity
14	1.0
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10	0.0001
9	0.00001
8	0.000001
7	0.0000001
6	0.00000001
5	0.000000001
4	0.0000000001
3	0.00000000001
2	0.000000000001
1	0.0000000000001
0	0.00000000000001

Calculating activity

- If pH = 8.0, solve for (H+)

  $pH = -\log (H^+)$

  $8 = -\log (H^+)$

  $-8 = \log (H^+)$

  $10^{-8} = 10^{\log (H+)}$

  Since log is exponential power at base 10, $10^{\log}$ cancels out to a value of 1

  $(H^+) = 10^{-8} = 0.00000001$

Soil pH

Typically between 5.0 and 8.5

Why do we care about soil pH?

- Reactions in soil are affected by pH
  - Weathering
  - Microbial activity
  - Elemental activity
- Extremes can be caustic
  - Strong acids burn living tissues, including plant roots
    - Rarely occurs (pH has to be much lower than normal)
  - Strong bases burn living tissues, including plant roots
    - Rarely occurs (pH has to be much higher than normal)
- Toxicities of other elements
- Deficiencies of nutrients

Near neutral soils (pH 6.5-6.9) are ideal for most plants and other organisms that live in soil.

In practical terms, there is not much difference between about pH 5.8 and 7.3

Formation

- Soils in semi-arid and arid zones tend to accumulate carbonates and other salt precipitates with alkaline pH.
- The source of these salts are weathered minerals and carbonic acid deposit from the air.
- They do not leave the system readily due to a lack of precipitation.

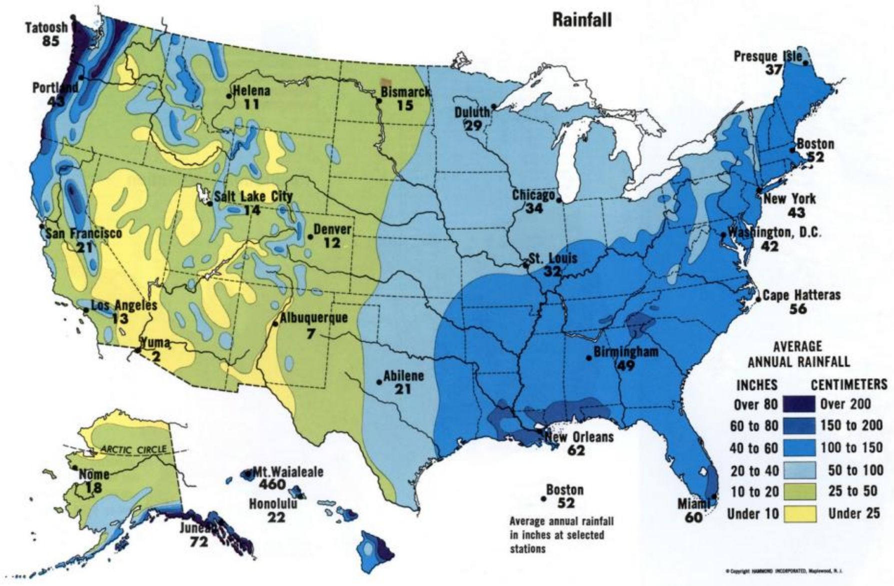
Formation

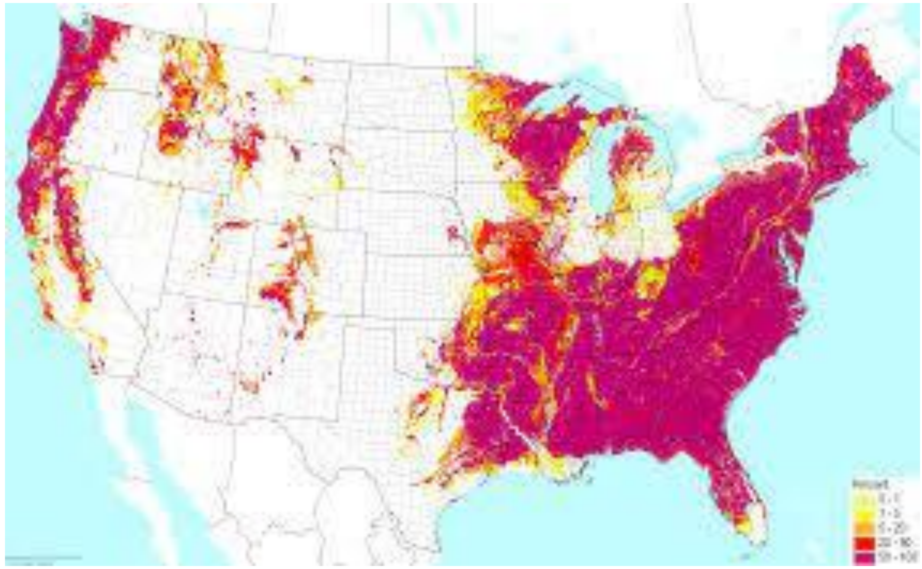
- In high rainfall areas, these salts are moved out of the soil into groundwater and to surface waters and eventually into the ocean. As the bases (Ca, Mg, Na, & K) are moved out, they are replaced on the CEC complex with H^+ from the water.
- Irrigation water typically does not act in the same way as it is generally high in dissolved salts that replace any that are lost with water movement through the soil.

Formation

- In addition to rainfall induced acidification,
  - Water combines with carbon dioxide to form carbonic acid.
    - $H_2O + CO_2 \leftrightarrow H_2CO_3$
  - Plants exude H^+ from their roots and acidify soil over time.
  - Ammonium based fertilizers (and some other types too) also acidify over time.
  - Acid rain deposition can also impact soil pH.

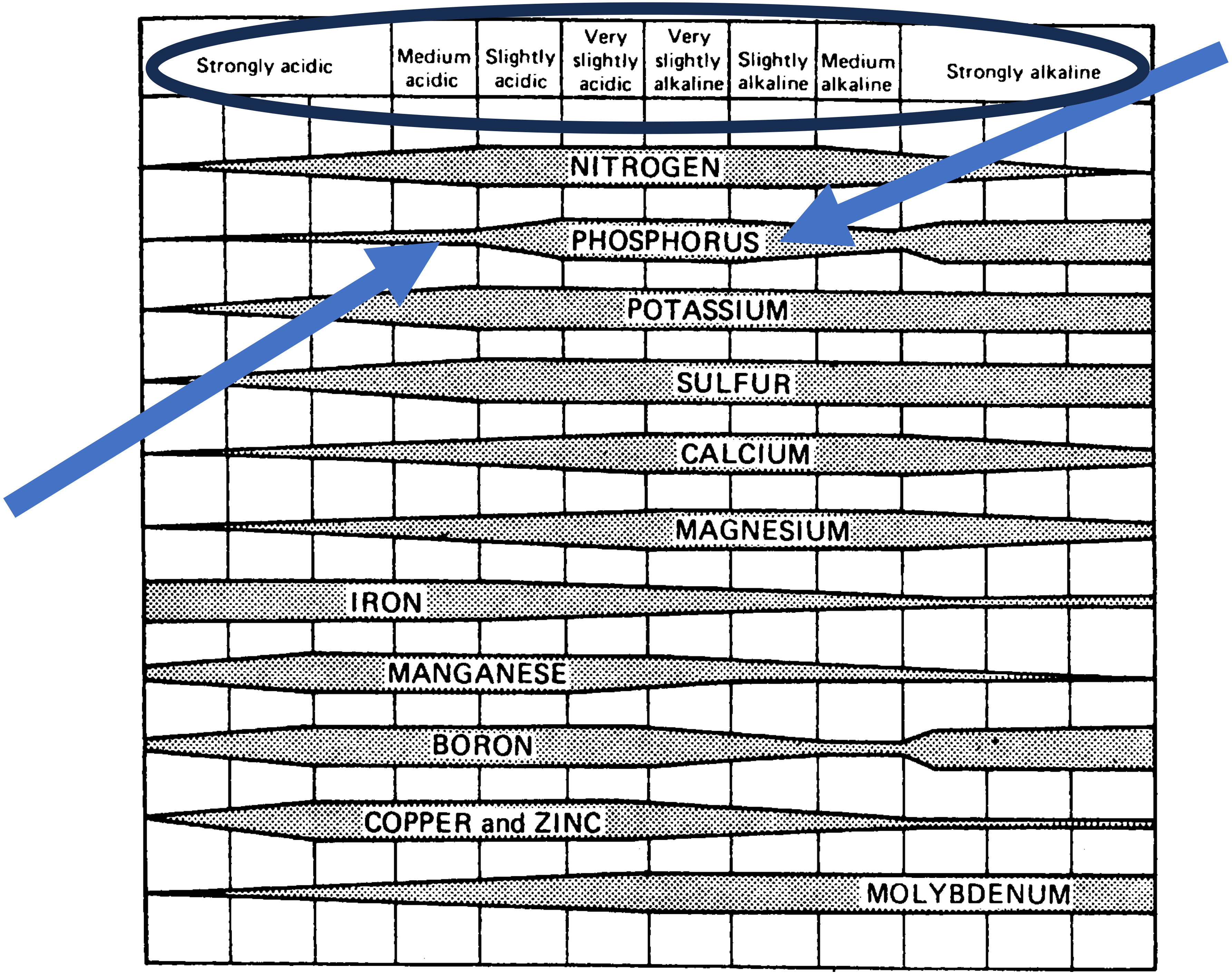
As a result, soil pH tends to mimic rainfall trends with low rainfall areas in the western U.S. having alkaline pH and high rainfall areas in the east acidic.





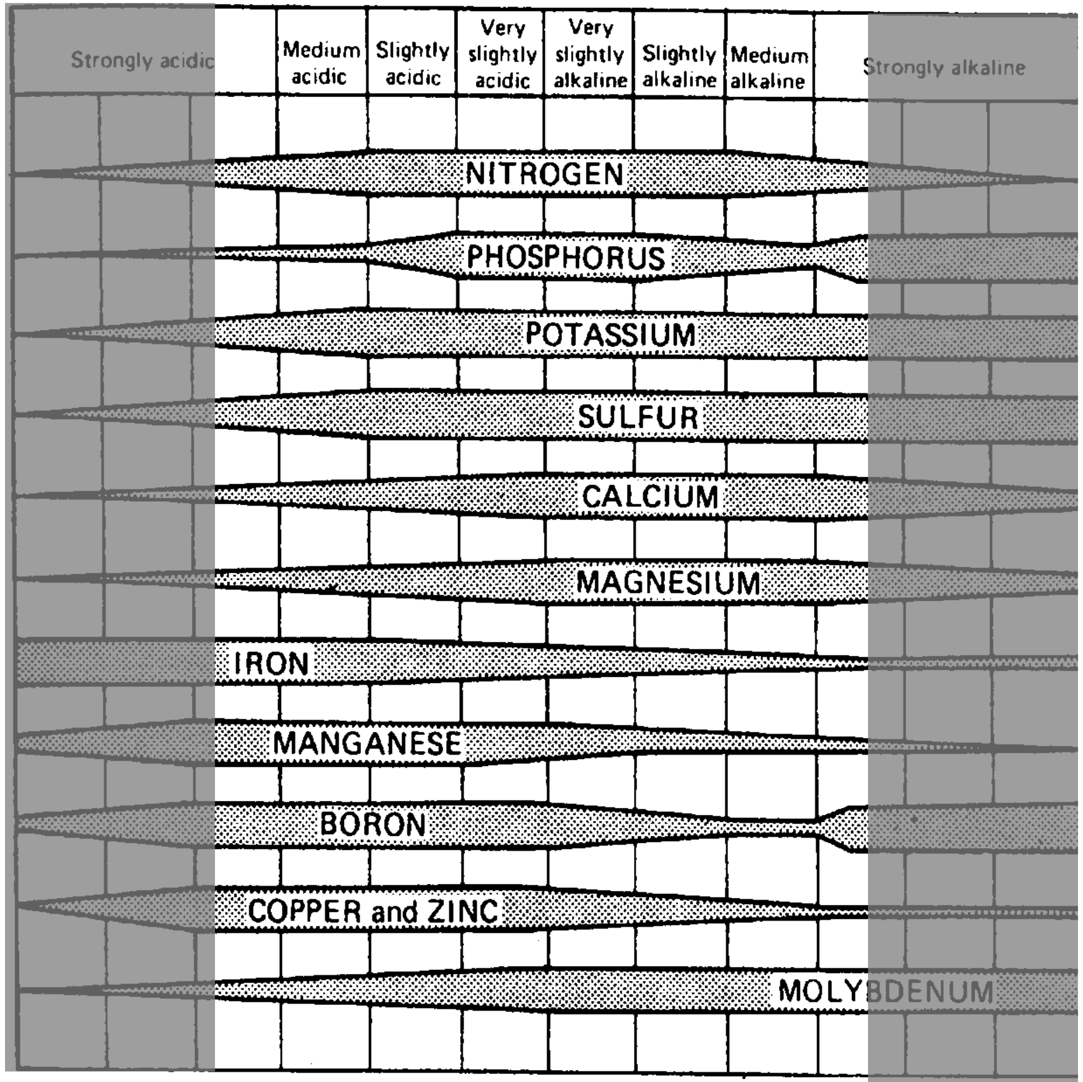
Alkaline soils (pH > 7)

The main problem of alkaline soils is nutrient availability.



Strongly acidic
Medium acidic
Slightly acidic
Very slightly acidic
Very slightly alkaline
Slightly alkaline
Medium alkaline
Strongly alkaline
NITROGEN
PHOSPHORUS
POTASSIUM
SULFUR
CALCIUM
MAGNESIUM
IRON
MANGANESE
BORON
COPPER and ZINC
MOLYBDENUM

Range common in soils is medium acidic to medium alkaline.



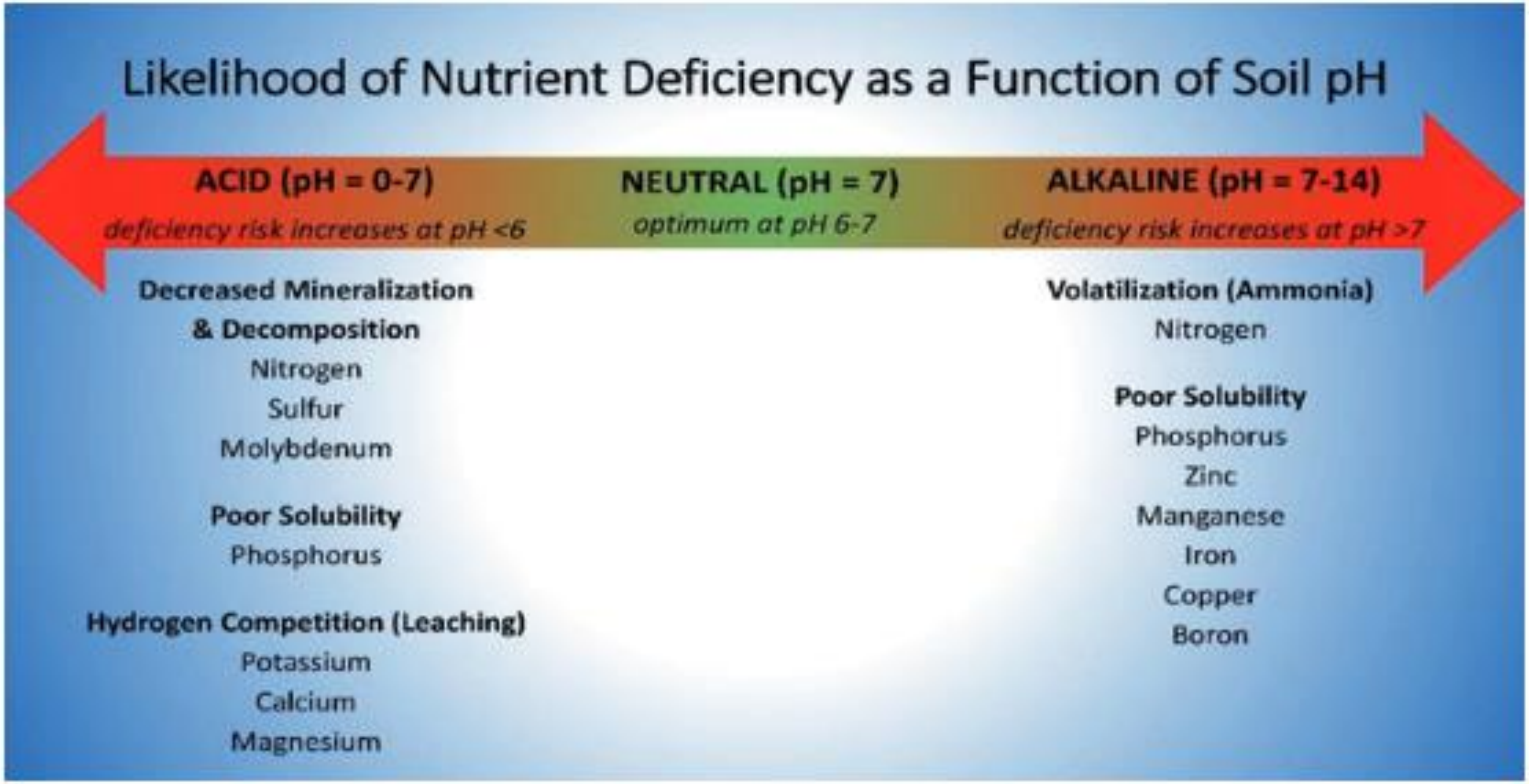


Fig. 8.2 Influence of soil pH on plant nutrient deficiencies

Hopkins B.G., Stark J.C., and Kelling K.A. 2020. Nutrient Management. *In* Stark J., Thornton M., Nolte P. *(ed) Potato Production Systems*. Ch. 8:155-202. New York, New York: Springer, Cham. DOI: https://doi.org/10.1007/978-3-030-39157-7_8 (ISBN978-3-030-39157-7)

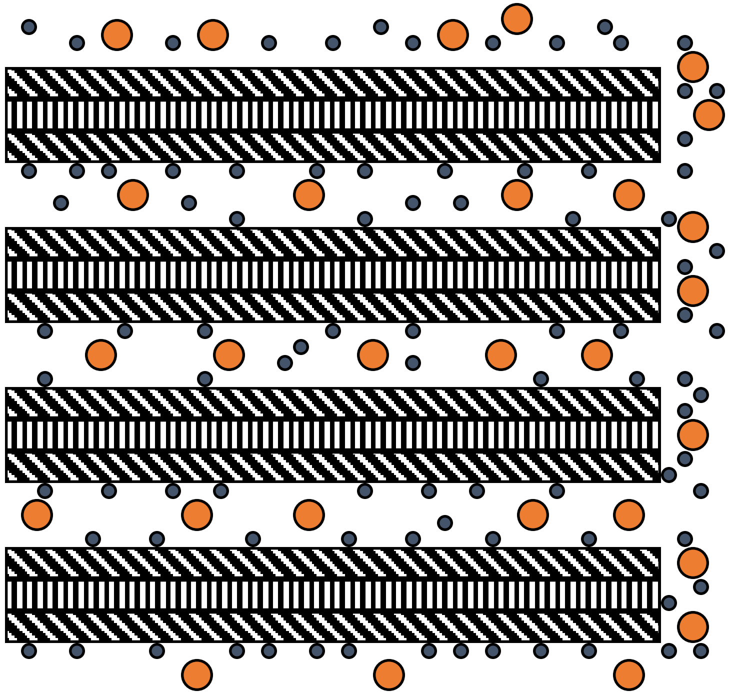
Soil Acidity

- Active acidity
- H^+ ions in the soil solution
- Reserve acidity
- H^+ ions on the soil exchange sites
- Buffering capacity
- -- resistance to pH change
- Limestone requirement increases with increasing CEC

Reserve Acidity

- [redacted]
- [redacted]
- [redacted]
- [redacted]

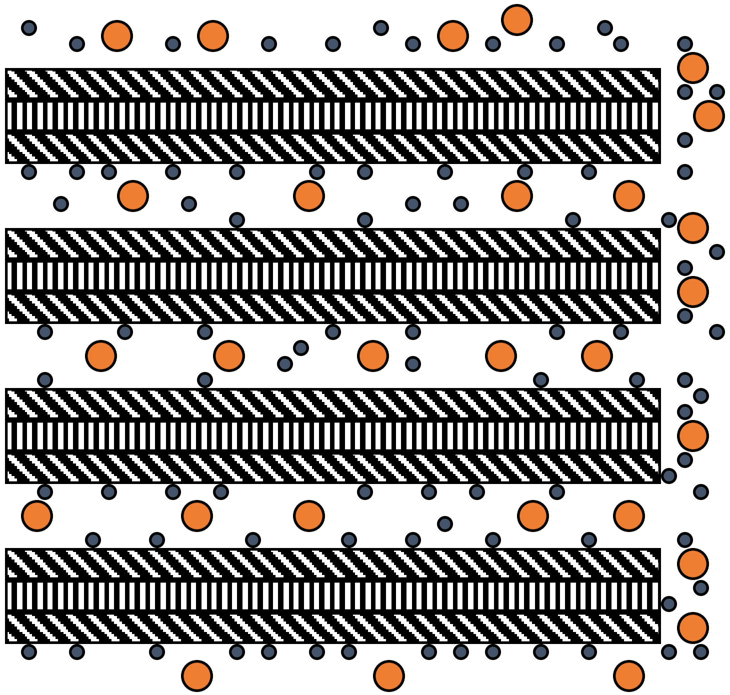
Reserve Acidity



Al ions

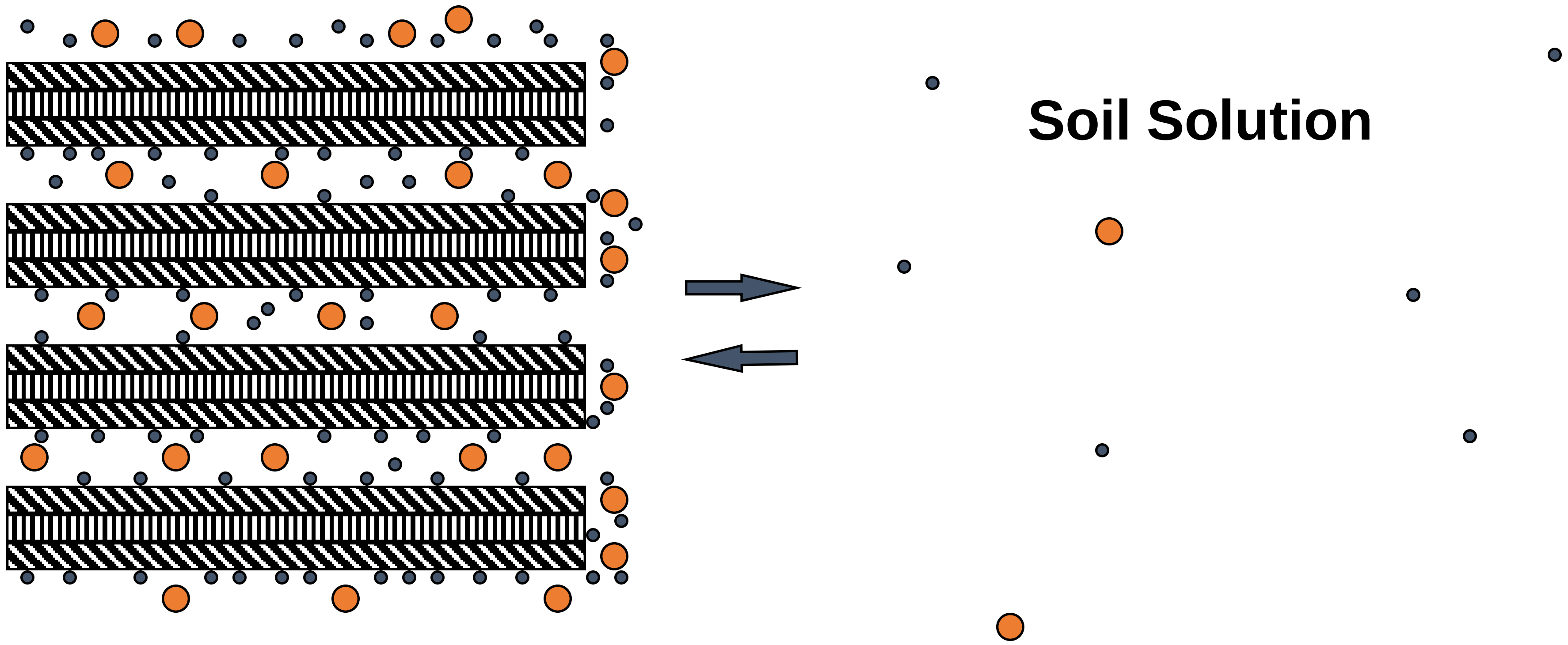
H^+ ions

Reserve Acidity

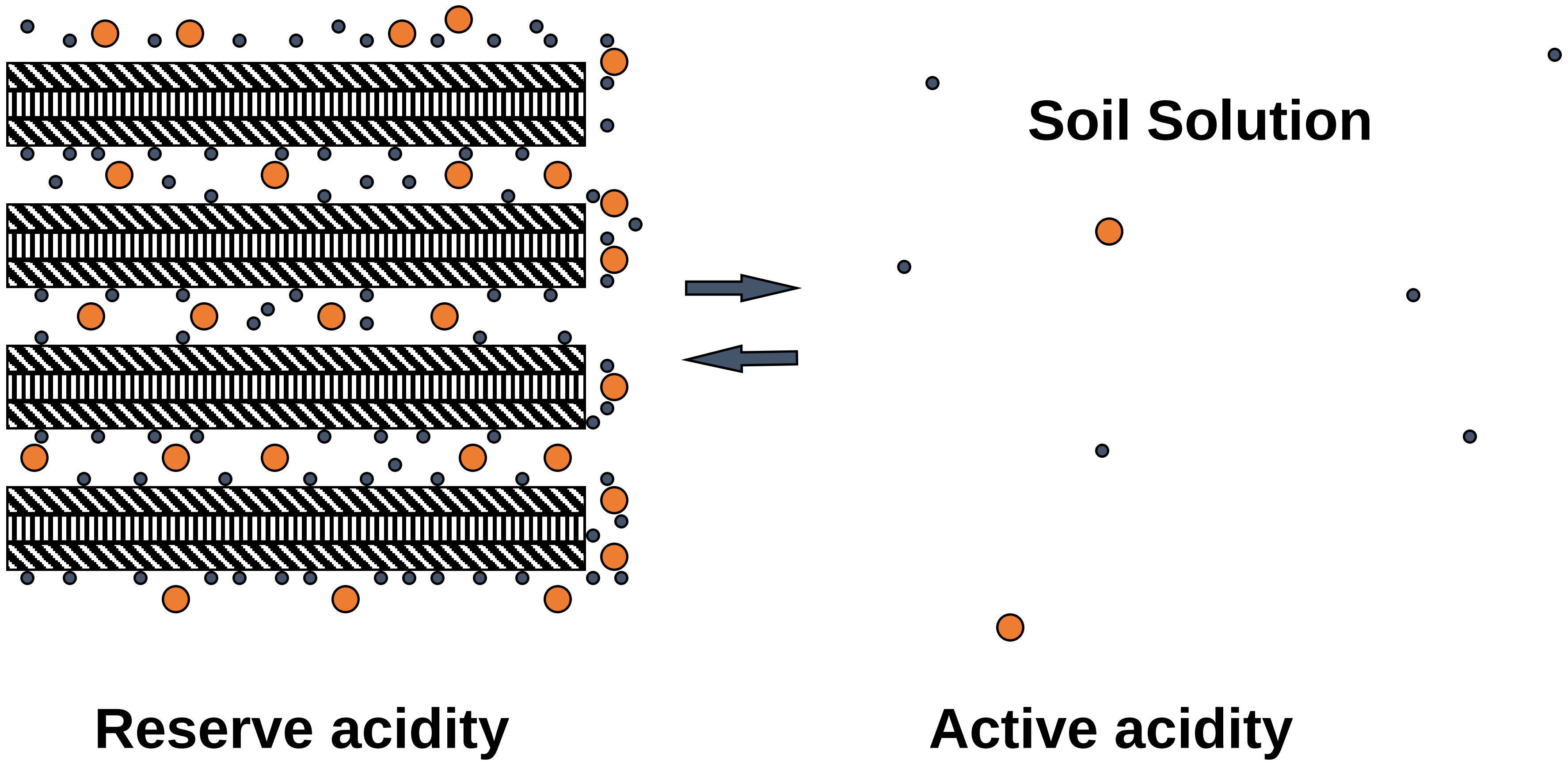


Soil Solution

Reserve Acidity

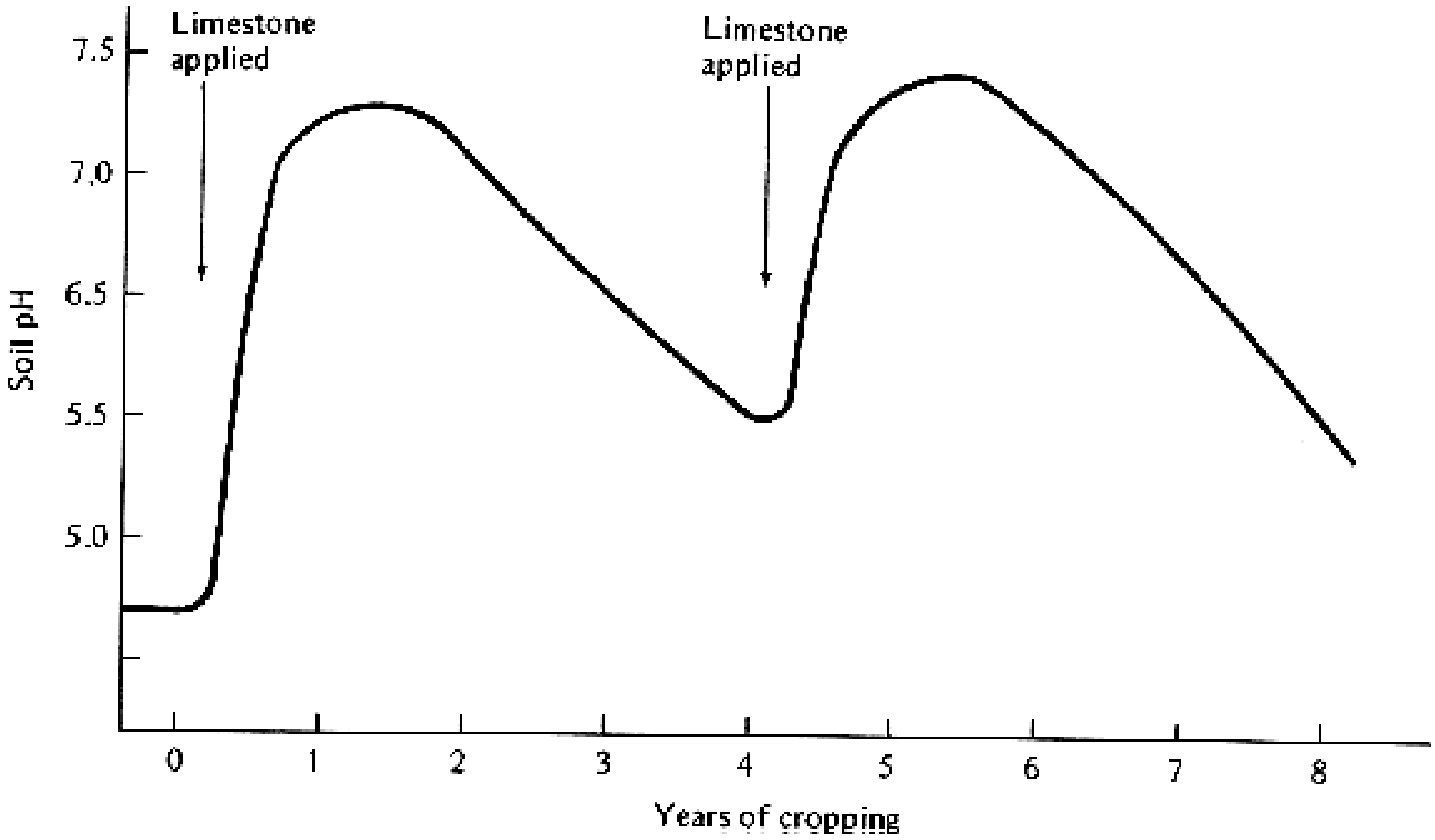


Reserve Acidity



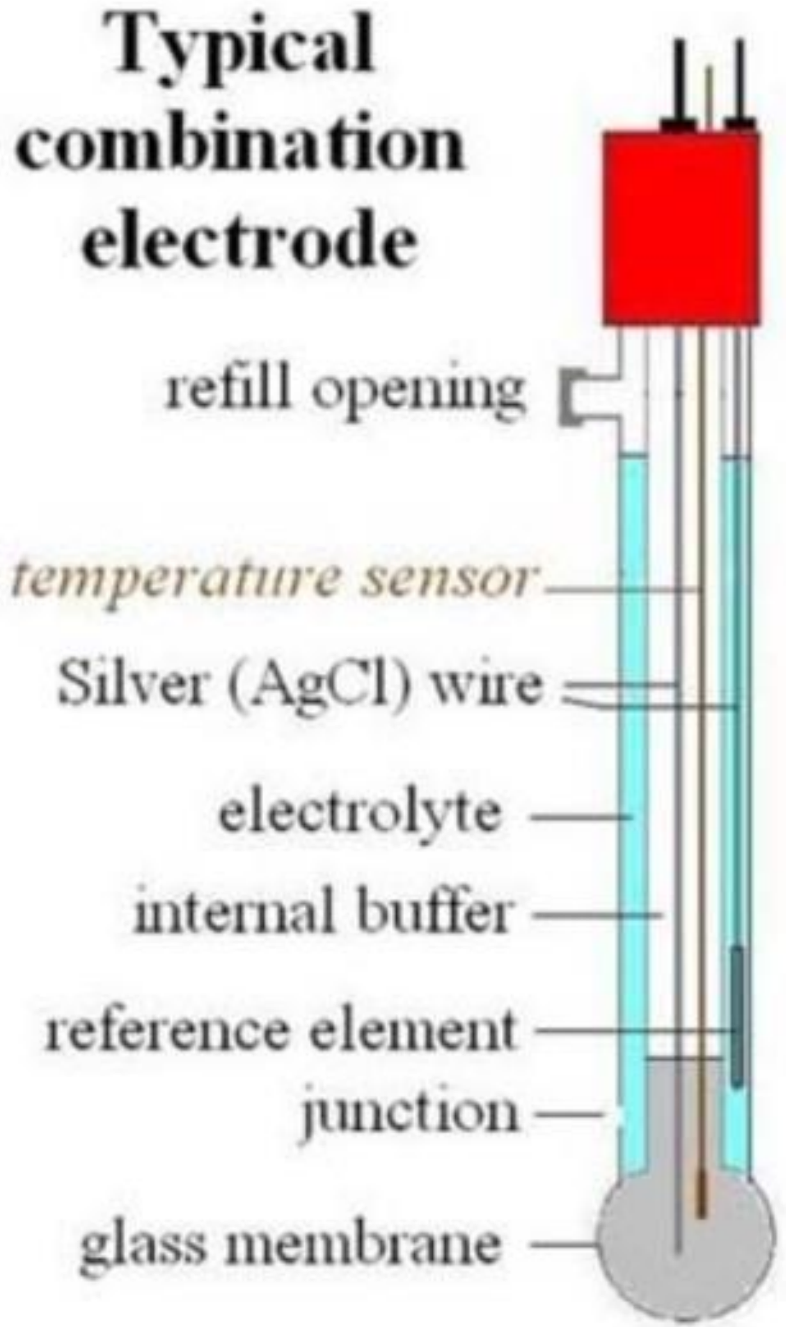
Liming action

- $CaCO_3 + 2H^+ \rightarrow H_2CO_3 + Ca^{2+}$
- $H_2CO_3 \rightarrow CO_{2(g)} + H_2O$
- 1. Raises soil pH
- 2. Precipitates Al, Mn, and Fe
- 3. Supplies Ca and Mg
- 4. Makes some nutrients more available to plants
- 5. Increases microbial activity

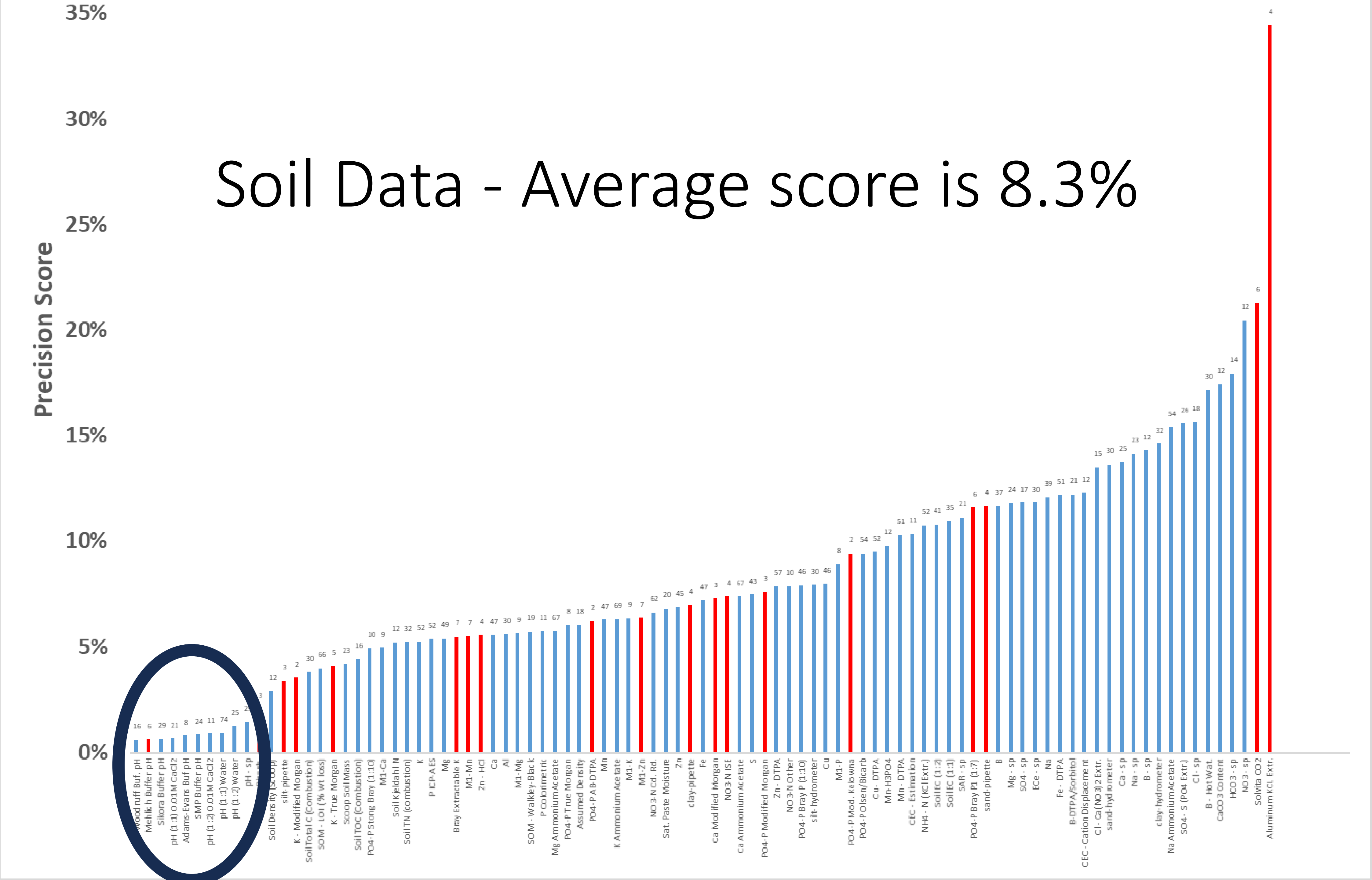

Limestone applied
Limestone applied
7.5
7.0
6.5
5.5
5.0
Soil pH
0
1
2
3
4
5
6
7
8
Years of cropping

Measuring pH

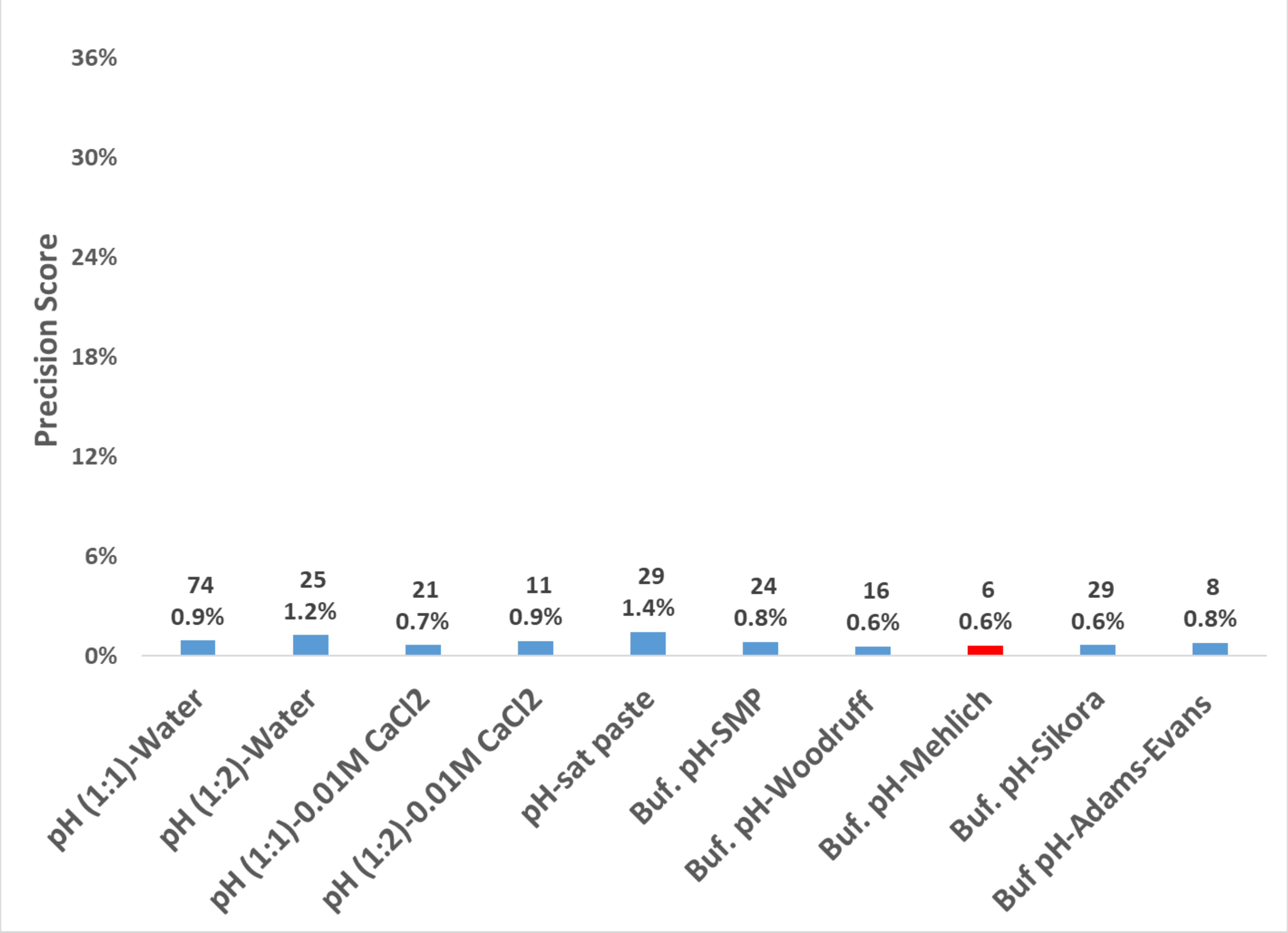
- Calibrating the pH probe
  - buffer solutions



- https://www.youtube.com/watch?v=PBTn4gTEbkU
- https://www.youtube.com/watch?v=vwY-xWMam7o


Soil Data - Average score is 8.3%
Precision Score
35%
30%
25%
20%
15%
10%
5%
0%
Woodruff Buf. pH
Mehlich Buffer pH
Sikora Buffer pH
pH (1:1) 0.01M CaCl2
Adams-Evans Buf pH
SMP Buffer pH
pH (1:2) 0.01M CaCl2
pH (1:1) Water
pH (1:2) Water
pH - sp
Soil Density (scoop)
silt-pipette
K - Modified Morgan
Soil Total C (Combustion)
SOM - LOI (% Wt loss)
K - True Morgan
Scoop Soil Mass
Soil TOC (Combustion)
PO4-P Stong Bray (1:10)
M1-Ca
Soil Kjeldahl N
Soil TN (combustion)
K
P ICP-AES
Mg
Bray Extractable K
M1-Mn
Zn - HCl
Ca
Al
M1-Mg
SOM - Walkley-Black
P Colorimetric
Mg Ammonium Acetate
PO4-P True Morgan
Assumed Density
PO4-P AB-DTPA
Mn
K Ammonium Acetate
M1-K
M1-Zn
NO3-N Cd. Rd.
Sat. Paste Moisture
Zn
clay-pipette
Fe
Ca Modified Morgan
NO3-N ISE
Ca Ammonium Acetate
S
PO4-P Modified Morgan
Zn - DTPA
NO3-N Other
PO4-P Bray P (1:10)
silt-hydrometer
Cu
M1-P
PO4-P Mod. Kelowna
PO4-P Olsen/Bicarb
Cu - DTPA
Mn-H3PO4
Mn - DTPA
CEC - Estimation
NH4 - N (KCl Extr.)
Soil EC (1:2)
Soil EC (1:1)
SAR - sp
PO4-P Bray P1 (1:7)
sand-pipette
B
Mg - sp
SO4 - sp
ECe - sp
Na
Fe - DTPA
B-DTPA/Sorbitol
CEC - Cation Displacement
Cl - Ca(NO3)2 Extr.
sand-hydrometer
Ca - sp
Na - sp
B - sp
clay-hydrometer
Na Ammonium Acetate
SO4 - S (PO4 Extr.)
Cl - sp
B - Hot Wat.
CaCO3 Content
HCO3 - sp
NO3 - sp
Solvita CO2
Aluminum KCL Extr.

pH

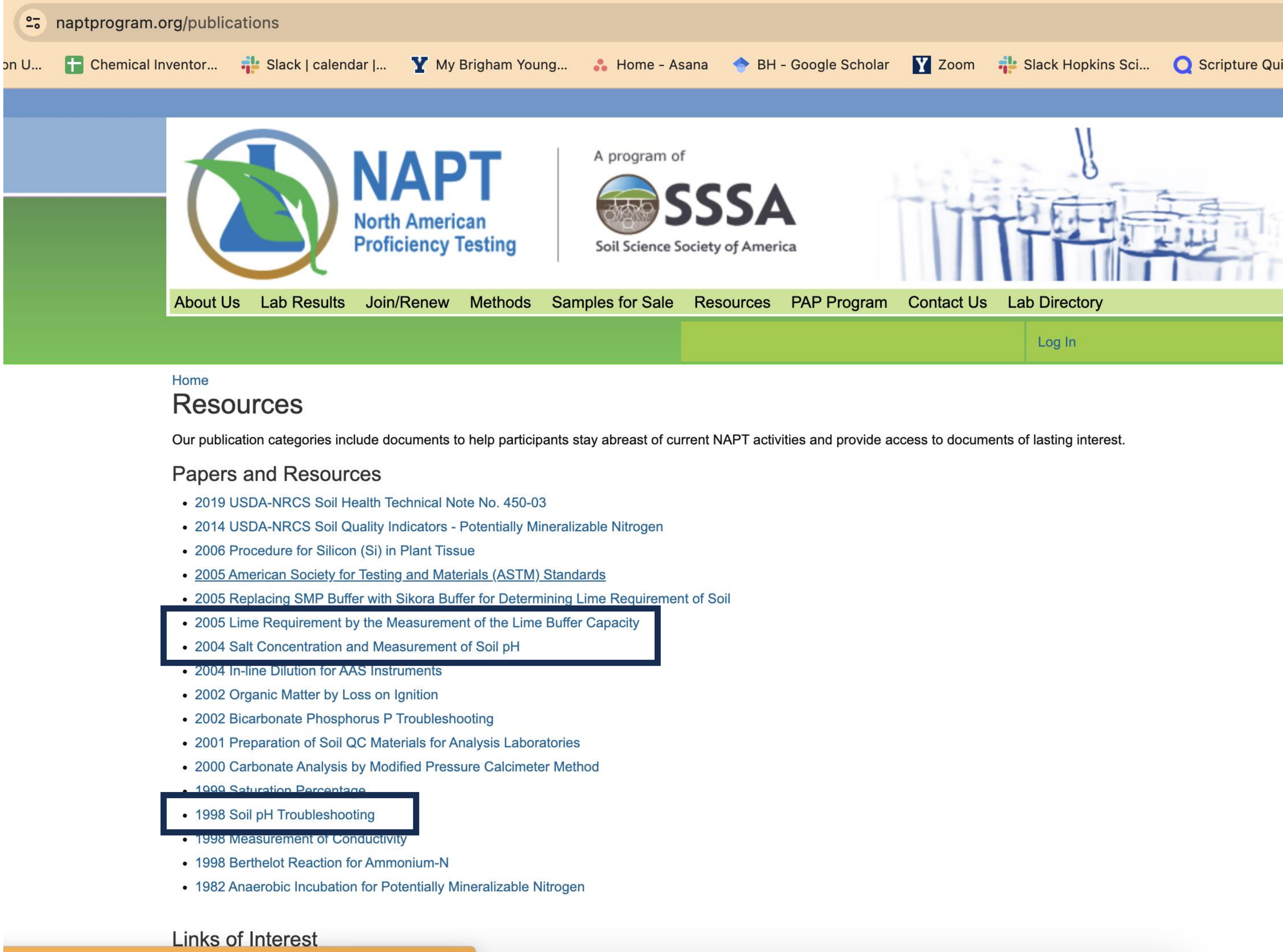


Precision Score
36%
30%
24%
18%
12%
6%
0%
74
0.9%
25
1.2%
21
0.7%
11
0.9%
29
1.4%
24
0.8%
16
0.6%
6
0.6%
29
0.6%
8
0.8%
pH (1:1)-Water
pH (1:2)-Water
pH (1:1)-0.01M CaCl2
pH (1:2)-0.01M CaCl2
pH-sat paste
Buf. pH-SMP
Buf. pH-Woodruff
Buf. pH-Mehlich
Buf. pH-Sikora
Buf pH-Adams-Evans

pH Troubleshooting

One of most difficult tests to troubleshoot

www.naptprogram.org
-click on “resources””



QA/QC

- Known Solution
  - Buffers (4, 7, and 10)
    - Calibrate
    - Recheck
      - <0.04 pH units
      - Equilibration <10 seconds
  - Solutions of varying salt concentrations (EC)
    - 0.1
    - 0.5
    - 1.0
    - 4.0

QA/QC

- Known Solutions
- Known Checks
  - Range of:
    - pH
    - salt concentrations
    - Buffering capacity (CEC - texture/OM)

Known Check Soil Samples

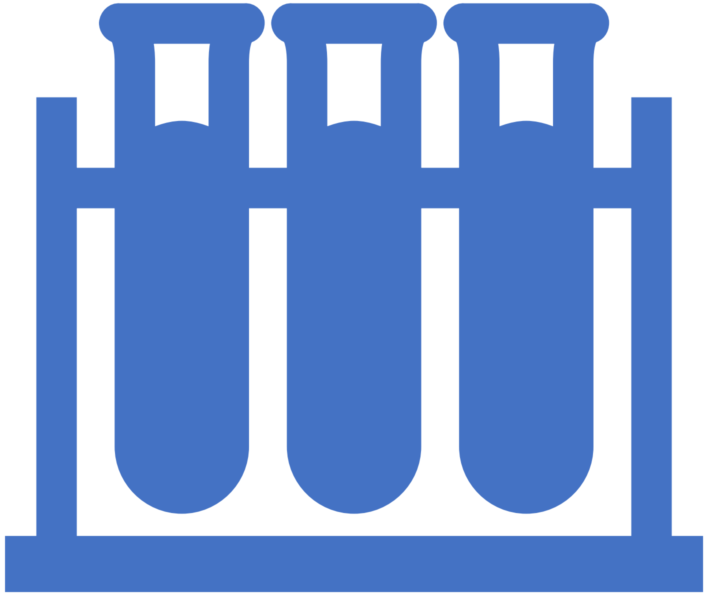
Soil	pH	Texture	CEC	Salts (EC)
1	4.9	Sand	2	0.1
2	5.2	Clay Loam	32	0.1
3	6.6	Loam	25	0.3
4	7.3	Sandy Loam	8	1.4
5	8.2	Silt Loam	28	4.2

QA/QC

- Known Solutions
- Known Checks
- Duplicates
  - With different electrodes/meters
- Blind Samples
  - Proficiency testing
- Double Blind

Case Study 1

- Known Checks for pH were all out of range (high and low)
- Duplicates were >10% error
- Buffer pH was within range
- Known solution at low EC was out of range
- Cause?
  - Bad electrode



Case Study 2

- All QC was within range, but clients calling in with complaints.
- Double Blind were off by as much as 2.2 pH units
- Cause?
    - Analyst was hurrying through customer samples and slowing down for QC samples.

Case Study 3

- QC mostly ok, but robotic data was bad for electrode #3
- Cause?
    - Junction had salt buildup on it

Case Study 4

- QC samples out of range at end of run, biased to neutral
- Duplicates were all >10% error (duplicates were run at end of batch)
- Cause?
    - Dispenser out of calibration at end of run

Case Study 5

- Known Check samples out of range at end of run, biased high
- Duplicates and Known Solutions and Proficiency Samples were all within range
- Cause?
  - Samples were scooped night before and left open to the air and custodians spilled ammonia solution on floor

pH

- Know your equipment
- Store electrodes properly
- Minimize abrasion on electrode
- Evaluate cables
- Dispensor volume
- Correct scoop size and technique
- Meter instability
- Static electricity
- Junction location to liquid surface
- Stirrer contact/speedSlurry or supernatant
- Duplicates with different probes
- Residue buildup
- Flow rate of the liquid junction
- Rinsing?
- Stirring while measuring?
- Contamination (NH3)

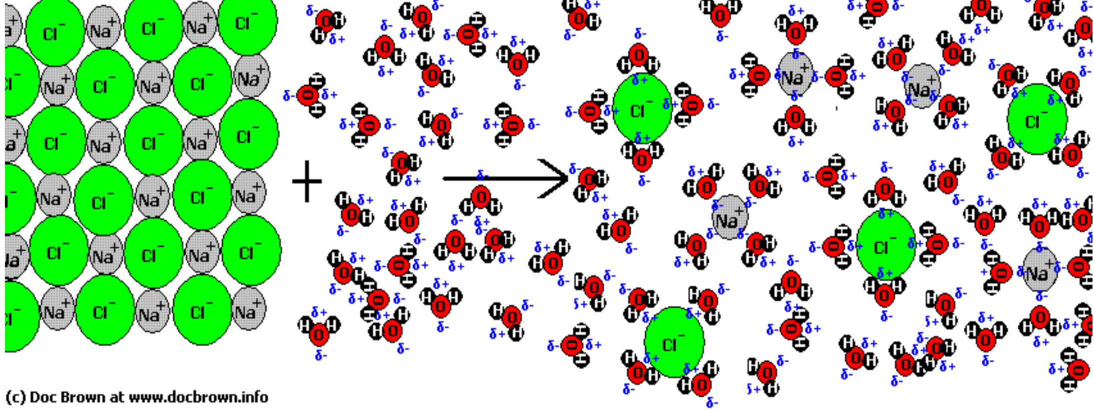
Troubleshooting

- Difficult
  - Buffers vs. Soil
    - High Buffer/High Salts (EC) vs. distilled water - soil in between
      - Especially problematic with high water to soil ratios . . . Rare problems with buffer pH
      - Salt pH the answer? (0.01 $CaCl_2$ or 1 M KCl
  - Multiple probes (need duplicates)
  - Varying time (manual techniques)
  - Need multiple check samples with varying pH and salts
  - Equilibration time
  - Stirring
  - Static electricity
  - Air, solution, and rinse water temperatures
  - Junction flow rates (quartz, asbestos, ceramic, frit, annular, sleeve) – need rapid flow
  - Plugged junction
  - Poor response time (<10 seconds to go from pH 4 to 7)
  - Span error should be <0.05 pH unit
  - Reproducibility on the sample sample should be <0.03 pH unit
  - Improper storage

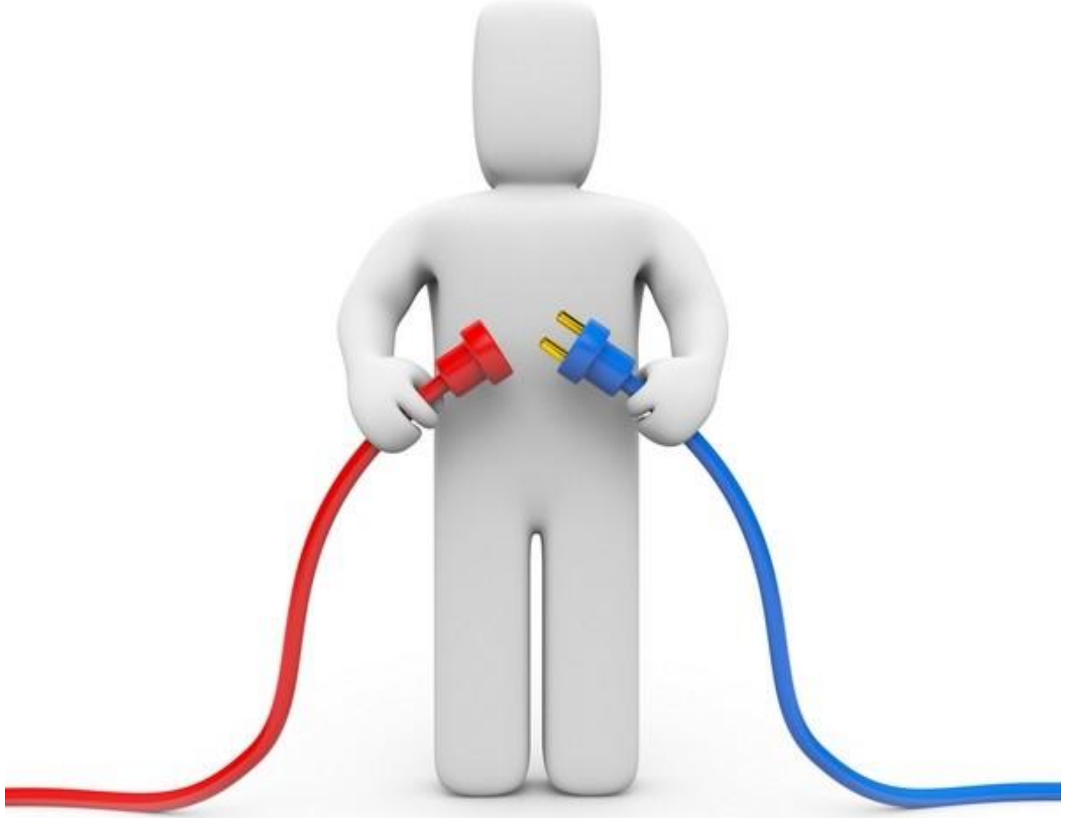
Questions?

naptcoordinator@soils.org

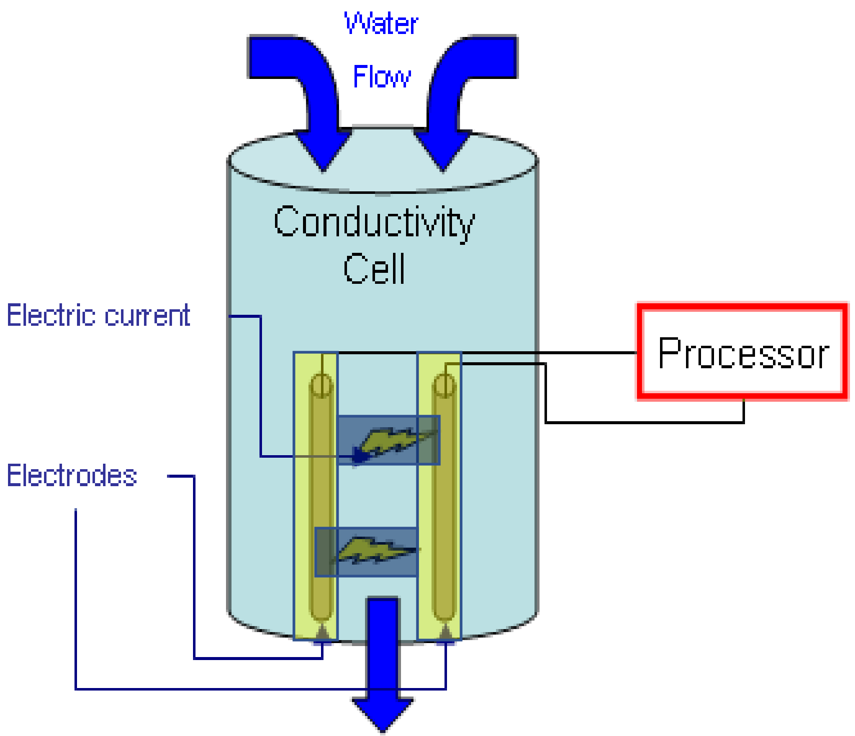
Electrical Conductivity (EC)



- Electrical conductivity is the measure of a substances ability to conduct (transport) an electric current.
- Ions, because of their positive and negative charges, conduct electrical currents very well
- Water conducts electricity poorly, but when ions are dissolved in solution conductivity increases
- Therefore EC is proportional to the amount of ions in solution
    - EC indicates how many salts are in the soil



Electrical Conductivity (EC)



- Conductivity Cells measure EC
- How Conductivity Cell's work
  - Measures EC with two electrodes at a specific distance apart
  - The electrodes change charges
  - The ions in the solution travel electrode to electrode as the charges change
  - The amount of charge that the ions carry to the electrodes is measured
    - The more ions in solution, the larger amount of electrical charge that is carried
- Normal soils have an EC< 4 dS/m